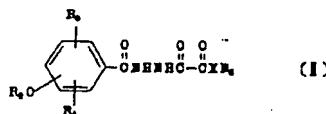


Title

Organic material composition

Patent Claim

Organic material composition containing at least one compound represented by the following formula (I) or (II) which has stability with respect to the effects of light, or which has resistance to contact with heavy metals.



(wherein

R₁ denotes a group which is the residue of an aromatic nitrogen-containing ring,

R₂ denotes hydrogen or a group which is the residue of an aliphatic hydrocarbon,

R₃ and R₄, which may be the same or different, respectively denote hydrogen or a group which is the residue of an aliphatic hydrocarbon,

X denotes -O-, -NH-, -HNH-, or -NHN=C(R₆)-,

R₅ denotes hydrogen, or a group which is the residue of an aliphatic or aromatic hydrocarbon,

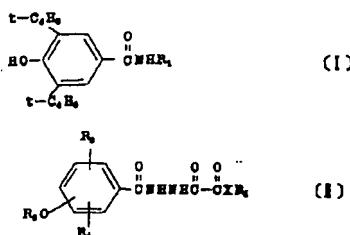
R₆ denotes a group which is the residue of an aliphatic or aromatic hydrocarbon, or

forms a ring which includes R₅ together with the carbon atom to which it is bonded directly)

Detailed Description of the Invention

This invention relates to an organic material composition which is stable with respect to the effects of light, or which has resistance to contact with heavy metals.

In more detail, this invention provides an organic material composition which is stable with respect to light and heavy metals, wherein at least one compound represented by the following formula (I) or (II) is included in an organic material which readily decomposes or deteriorates due to the effects of light, or which readily decomposes or deteriorates due to contact with heavy metal.



(wherein

R₁ denotes a group which is the residue of an aromatic nitrogen-containing ring,
R₂ denotes hydrogen or a group which is the residue of an aliphatic hydrocarbon,
R₃ and R₄, which may be the same or different, respectively denote hydrogen or a group
which is the residue of an aliphatic hydrocarbon,
X denotes -O-, -NH-, -NHNH-, or -NHN=C(R₆)-,
R₅ denotes hydrogen, or a group which is the residue of an aliphatic or aromatic hydrocarbon,
R₆ denotes a group which is the residue of an aliphatic or aromatic hydrocarbon, or
forms a ring which includes R₅ together with the carbon atom to which it is bonded directly)

The problem with organic materials of hydrocarbon oil, synthetic resin, rubber and the like is that they are generally sensitive to ultraviolet radiation, or are also sensitive to contact with heavy metals, and decomposition or deterioration occurs due to the effect of these, causing discoloration of the organic material, alteration of mechanical strength and the like, so that durability in long-term use cannot be obtained.

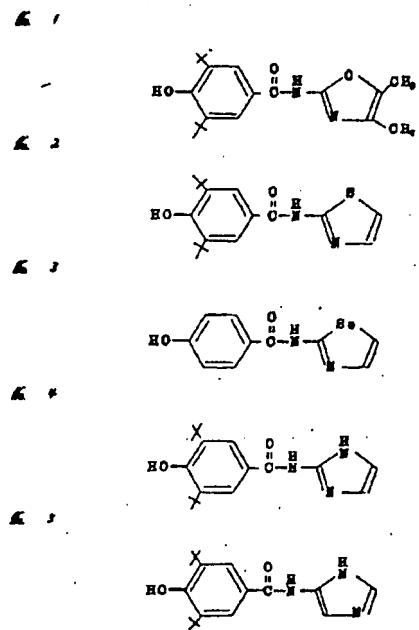
In the prior art, various ultraviolet absorbers or agents which make heavy metals inactive have been used in order to obtain resistance to this deterioration or decomposition, but although these provide an effect to some extent, such photostabilisers and heavy metal inactivators themselves have poor stability with respect to heat, oxidation in air, nor do they have excellent dispersibility, and so they are not satisfactory.

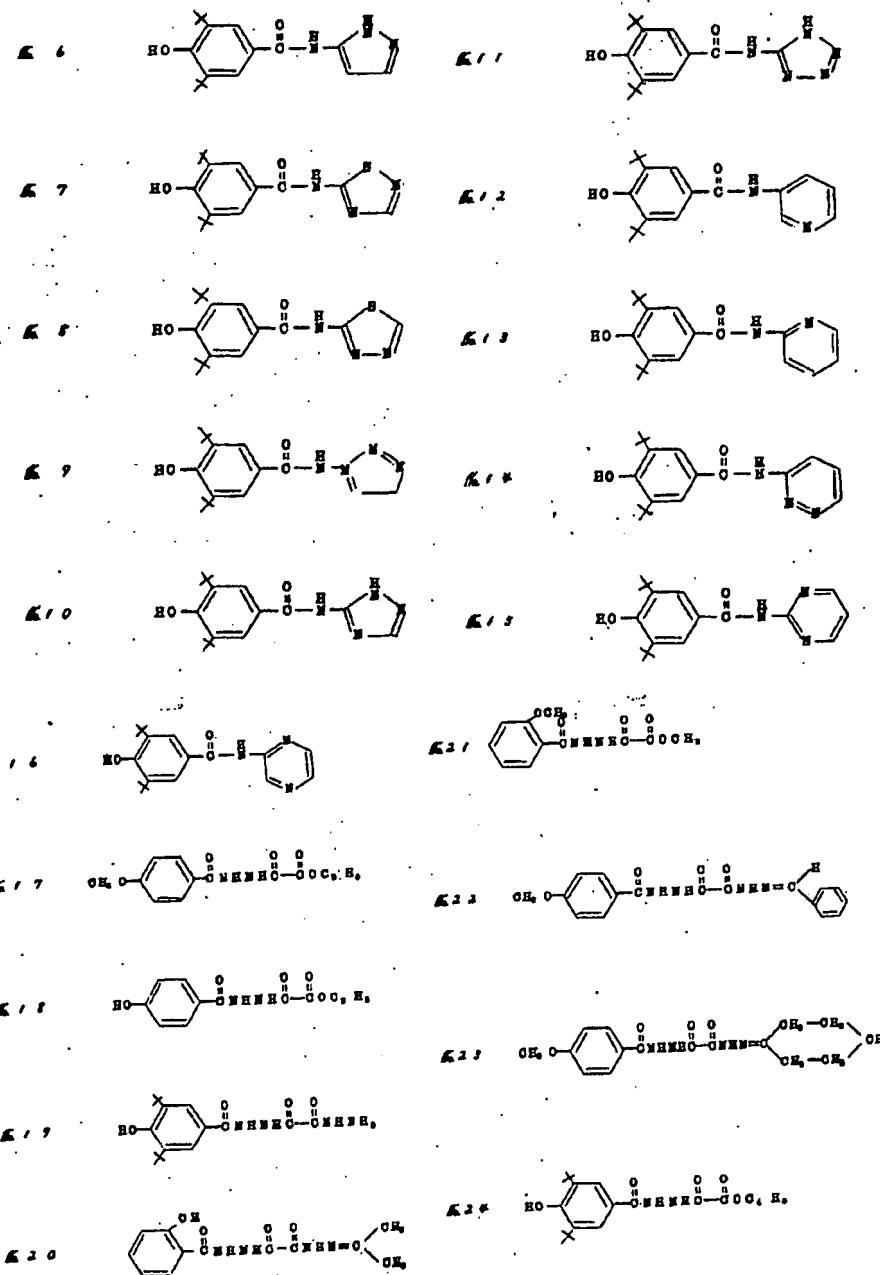
The object of this invention is to investigate such problems and provide stable organic material compositions which are useful over a long period of time, by improving the dispersibility and stability with respect to heat and atmospheric oxidation of the stabilizers and heavy metal inactivators themselves.

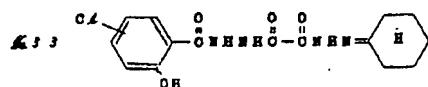
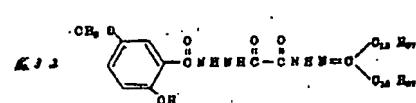
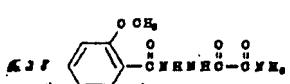
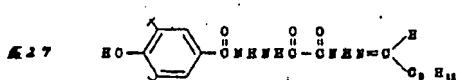
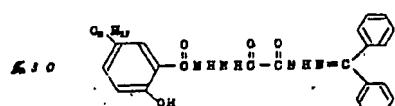
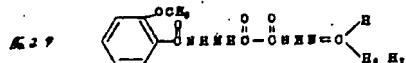
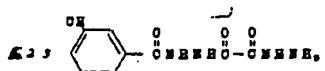
The compounds of the following Table 1 are examples provided as representative compounds

shown by the aforesaid general formulae.

Table 1

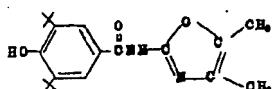






The production process of embodiments of the photostabilizers and metal inactivators for organic materials of this invention can be illustrated by the following synthesis examples.

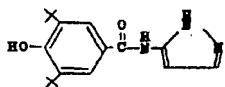
However, this invention is not restricted to the synthesis examples reported here.

Synthesis Example 1 (synthesis of the compound No. 1)

A mixture of 5-amino-3,4-dimethylisoxazole 11g, phenyl 3,5-di-t-butyl-4-hydroxybenzoate 36g and dioxane 50cc was reacted under reflux of the solvent for 7 hours. The reaction material formed a viscous semi-solid, however, ethanol 120 cc was added to this while it was still hot, and it was cooled while stirring well, the product was filtered off and washed several times with ethanol, and a white powder 19.2 g was obtained.

Verification of the product was performed by infrared absorption spectrum and atomic analysis.

Product analysis values	C 70.03%	H 8.11%	N 8.07%
calculated values	C 69.74	H 8.19	N 8.13

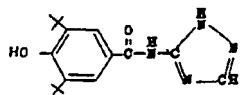
Synthesis Example 2 (synthesis of the compound No. 6)

A mixture of 3-amino-pyrazole 8.5g, phenyl 3,5-di-t-butyl-4-hydroxybenzoate 36g and dimethylformamide 70cc was heated and stirred at 150°C under a flow of nitrogen for 6 hours. After the reaction had ended, the mixture was left to stand overnight, the precipitated material which deposited was collected by filtration, washed twice with hot ethanol 50cc, and a white powder 7.8 g was obtained.

Verification of the product was performed by infrared absorption spectrum and atomic analysis.

Product analysis values	C 68.71%	H 7.78%	N 13.29%
calculated values	C 68.54	H 7.99	N 13.32

Synthesis Example 3 (synthesis of the compound No. 10)



A mixture of 3-amino-1,2,4-triazole 8.5g, phenyl 3,5-di-t-butyl-4-hydroxybenzoate 36g and dimethylformamide 60cc was heated and stirred at 150°C for 12 hours.

This was cooled to 80°C, ethanol 100cc was added and it was cooled, and the precipitated material which deposited was filtered, and washed several times with ethanol, and a white powder 24.1 g was obtained.

Verification of the product was performed by infrared absorption spectrum and atomic analysis.

Product analysis values	C 64.65%	H 7.58%	N 17.60%
calculated values	C 64.53	H 7.65	N 17.71

Synthesis Example 4 (synthesis of the compound No. 17)



A mixture of p-anisic acid hydrazide 14g, ethyl phenyl oxalate 21.5g and dioxane 15ml was heated and stirred for 12 hours under reflux of dioxane. Petroleum ether 50cc was added to the reaction mixture which had solidified on cooling, it was filtered and washed with ether.

This product was dissolved in benzene and filtered hot to remove insoluble material, cooled, and the precipitated material which deposited was collected, and a white powder was obtained. Yield 14.8 g.

Verification of the product was by infrared absorption spectrum and atomic analysis.

Product analysis values	C 54.29%	H 5.09%	N 10.32%
calculated values	C 54.13	H 5.30	N 10.52

Synthesis Example 5 (synthesis of the compound No. 23)



The product of Synthesis Example 4 12g, hydrazine hydrate (80%) 3.5g and ethanol 30cc were reacted for 3 hours at 60°C, then made to a dry solid by removal of solvent. Then ethanol 30 cc and cyclohexane 6g were again added, left to stand overnight on a warm bath.

After cooling, the precipitate was filtered and washed with ethanol, and a white powder 7g was obtained.

Verification of the product was by infrared absorption spectrum and atomic analysis.

Product analysis values	C 58.05%	H 5.98%	N 6.77%
calculated values	C 57.82	H 6.07	N 6.86

In this invention, the organic materials to be stabilized with respect to the effects of light and with respect to contact with heavy metals are mainly polymer materials, for example polyolefin, preferably α -olefin polymer, for example polypropylene, optionally crosslinked polyethylene, polyisobutylene, polymethylbutene-1, polymethylpentene-1, polypentene-1, polyisoprene, polybutadiene; copolymer of monomers, for example ethylene/propylene copolymer, propylene/butene-1 copolymer, propylene /polyisobutylene copolymer, styrene/polybutadiene copolymer; terpolymer of ethylene and propylene with diene, for example hexadiene, dicyclopentadiene, or ethylidene-norbornene; mixtures of the aforesaid homopolymers, for example polypropylene and polyethylene, polypropylene and polybutene-1, polypropylene and isobutylene, and the like. Polypropylene or its mixtures, and copolymers having propylene units; copolymers and graft polymers of styrene and butadiene with acrylonitrile, acrylic acid, and methacrylic acid ester, optional vinyl ester or vinyl chloride; halogen-containing polymers such as polymers or copolymers of vinyl chloride, vinylidene chloride, vinylidene fluoride and the like; and condensation polymers for example polycarbonate, polyamide, polyester, polyacetal, polyphenylene oxide, polyurethane, polythioether, thioplastic, melamine resin, urea resin, phenol resin, carbacid (sic) resin, epoxy resin and the like are preferred. Furthermore, natural polymers, for example cellulose, wool, wood, silk, shoe leather, jute, hemp, fur, hair, leather, gelatin, glue, rubber; moreover, semi-synthetic materials, of cellulose esters, nitrocellulose, cellulose ethers, regenerated cellulose,

casein plastics; and in addition, perfume, soap, cream, dye, chemical bleach, detergent, cloth, paper and the like may be proposed.

Moreover, oils and waxes which have synthetic ester base may also be stabilized in accordance with this invention.

Moreover, in the organic material composition of this invention, their effect may be greatly increased by also using various additives as shown below. Moreover, they may provide new characteristics, greatly expanding the utility of the said material compositions.

They are especially phenolic oxidation inhibitors, for example 1-hydroxy-3-methyl-4-isopropyl benzene, 2,6-di-tert. butylphenol, 2,4-dimethyl-6-tert. butylphenol, 2,6-di-tert. butyl-4-methylphenol, 2,4-dimethyl-6-(2'-methylcyclohexyl)phenol, alkylated phenol, 2,5-di-tert. butylhydroquinone, 3-tert. butyl-4-hydroxyanisole, styrenated phenol, hydroquinone monobenzyl ether, 2,5-di-tert. amylhydroquinone, 2,6-di-tert. butyl-4-methoxyphenol, 4-hydroxymethyl-2,6-di-tert. butylphenol, 2,6-di-tert. butyl- α -dimethylamino-p-cresol, 4-hydroxy-3,5-di-tert. butylbenzylphosphonic acid ester, for example dimethyl or di octadecyl ester, or the ester of monohydric or polyhydric alcohol, for example methanol, ethanol, octadecanol, hexane diol, nonane diol, trimethylhexane diol, thiadiethylene glycol, trimethylol ethane or pentaerythritol, with β -4-hydroxy-3,5-di-tert. butylphenylpropionic acid as acid, 6-(4-hydroxy-3,5-di-tert. butylanilino)-2,4-dioctyl-thio-s-triazine, 2,4-bis(3,5-di-tert. butyl-4-hydroxyphenoxy)-6-octylthio-s-triazine, N-stearoyl-para-aminophenol, 4,4'-dihydroxydiphenyl, 4,4'-bis-(2,6-di-tert. butylphenol), 2,2'-methylene-bis-(4-methyl-6-tert. butylphenol), 2,2'-methylene-bis-(4-ethyl-6-tert. butylphenol), 4,4'-methylene-bis-(6-tert. butyl-O-cresol), 4,4'-methylene-bis-(2,6-di-tert. butylphenol), 2,2'-dihydroxy-3,3'-di(α -methylcyclohexyl)-5,5'-dimethyl-diphenylmethane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane, 4,4'-cyclohexylidene-bis-(2-cyclohexylphenol), 4,4'-butylidene-bis(6-tert. butyl-m-cresol), 2,2'-thio-bis-(4-methyl-6-tert. butylphenol), bis-(2-hydroxy-3,5-di-tert. butylphenyl)sulphide, 4,4'-thio-bis-(3-methyl-6-tert. butylphenol), 4,4'-thio-bis-(6-tert. butyl-O-cresol), bis-(3,5-di-tert. butyl-4-hydroxybenzyl)-malonic acid ester, for example di-dodecyl ester, di-octadecyl ester and 2-dodecyl-mercapto-ethyl ester and p-tert. octylphenyl ester, 1,1-bis(4-hydroxy-2-methyl-5-tert. butylphenyl)-3-dodecylmercapto-butane, 2-(3-methyl-4-hydroxy-5-tert. butylbenzyl)malonic acid dioctyl ester, s-(3,5-dimethyl-4-hydroxyphenyl)-thioglycollic acid octadecyl ester, tris(3,5-di-tert. butyl-4-hydroxybenzyl)isocyanurate, tris(3,5-di-tert. butyl-4-

hydroxyphenyl(propionyloxyethyl)isocyanurate, 2,6-bis-(2'-hydroxy-3-tert. butyl-5'-methylbenzyl)-4-methylphenol, 1,1,3-tris-(2'-methyl-4'-hydroxy-5'-tert. butylphenyl)-butane, 1,3,5-tris(3',5'-di-tert. butyl-4'-hydroxybenzyl)-2,4,6-trimethylbenzene, tris-(3,5-di-tert. butyl-4-hydroxyphenyl)phosphate, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2,2,2]-octane-3-(3,5-di-tert. butyl-4-hydroxyphenyl)-propionate, 1,3,5-tris(3,5-di-tert. butyl-4-hydroxyhydrocinnamoyl)hexahydro-s-triazine, tris(3,5-di-tert. butyl-4-hydroxyphenyl(propionyloxyethyl)isocyanurate and the like.

Phosphite oxidation inhibitor is for example diphenyl phosphite, triphenyl phosphite, tris-nonylphenyl phosphite, tridecyl phosphite, tris(2-ethylhexyl)phosphite, tributyl phosphite, dilauryl acid phosphite, dibutyl acid phosphite, tris(dinonylphenyl) phosphite, trilauryl trithio phosphite, trilauryl phosphite, bis(neopentylglycol) 1,4 cyclohexane dimethylene phosphite, distearyl pentaerythritol di phosphite, diisodecyl pentaerythritol di phosphite, diphenyl acid phosphite, tris(lauryl-2-thioethyl)phosphite, tris(mono, di mixed nonylphenyl)phosphite, hydrogenated-4,4'-isopropylidene diphenol polyphosphite, diphenyl bis[4,4'-n-butylidene bis(2-tert. butyl-5-methylphenol)]thiodiethanol diphosphite, bis(octylphenyl)-bis[4,4'-n-butylidenebis(2-tert. butyl-5-methylphenol)]1,6-hexane-diol diphosphite, phenyl 4,4'-isopropylidenediphenol pentaerythritoldiphosphite, phenyl diisodecyl phosphite, tetra tridecyl-4,4'-n-butylidenebis(2-tert. butyl-5-methylphenol) diphosphite, tetra tridecyl-1,1,3-tris(2'-methyl-5'-tert. butyl-4'-hydroxyphenyl)butane diphosphite, tetra (C₁₂-C₁₈-mixed alkyl)4,4'-isopropylidenediphenyl diphosphite, tris(4-hydroxy-2,5-di-tert. butylphenyl)phosphite, tris(4-hydroxy-3,5-di-tert. butylphenyl)phosphite, 2-ethylhexyl diphenyl phosphite and the like.

Amine type oxidation inhibitors are for example phenyl-1-naphthylamine, phenyl-2-naphthylamine, N,N'-diphenyl-p-phenylene diamine, N,N'-di2-naphthyl-p-phenylene diamine, N,N'-di tert. butyl-p-phenylene diamine, 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline, 6-dodecyl-2,2,4-trimethyl-1,2-dihydroquinoline, mono- and di-octyliminodibenzyl, polymeric 2,2,4-trimethyl-1,2-dihydroquinoline and the like.

Sulphur type oxidation inhibitors are for example β -thio-dipropionic acid esters, such as ethyl, lauryl, stearyl, myristyl or tridecyl esters, 2-mercaptop-benzimidazole salts, for example zinc salt, diphenyl thiourea, stearyl-(3,5-dimethyl-4-hydroxybenzyl)thioglycolic acid ester, thiadipropionic acid, phenothiazine, tetrakis(β -dodecylthiopropionyloxymethyl)methane and

the like.

As metal soap used in this invention, all metal salts usually used are proposed, and soaps of Cd, Ba, Zn, Ca, Mg, Sr, Pb, Sn, K, Na or the like are included in these.

Moreover, the general term 'metal soap' in this invention includes compounds such as organic tin mercaptide compounds, metal phenates, metal complexes of keto acids, and the like.

Generally, when metal soap is used as stabilizer, in many cases, an organotin stabilizer, lead soap or the like is used alone, but there are also many cases in which soaps of two or more of Cd, Ba, Zn, Ca, Mg, Sr, K, Na or the like are used together. For example many combinations such as Cd-Ba, Cd-Ba-Zn, Ba-Zn, Ca-Zn, Ca-Mg, Ca-Mg-Zn, Cd-Ba-organotin, organotin-Ba, organotin-Ca, Cd-Ba-Pb, Zn-Sr, Ca-Sr, K-Zn, Na-Zn or the like which satisfies the objective of the use may be proposed. As for the organic material composition in accordance with this invention, a combination of metal soaps or a single metal salt satisfying the objective can be chosen from many metal soaps groups.

Furthermore, non-toxic organic materials can be obtained by selected non-toxic ones from the aforesaid commonly used metal soaps, to obtain non-toxic organic materials with good thermal stability.

In addition, for example plasticiser, epoxy stabilizer, organic chelator, pigment, filler, foaming agent, static inhibitor, metal inactivator, nucleator, fogging inhibitor, plate-out inhibitor, surface processor, lubricant, flame retardant, light stabilizer, fluorescer, anti-mould agent, fungicide, non-metal stabilizer, epoxy resin, boric acid ester, light moderator, thiourea derivative, processing aid, separating agent, reinforcing agent and the like may be included as required.

In the following, this invention is explained more specifically by examples. However, this invention is not limited by the examples shown subsequently.

Example 1

polyvinyl chloride 100 parts

DOP	50 parts
*Mark AC143	1 part
stearic acid	0.3 parts
test material (Table 2)	0.1 parts

* Adeka Argus company. Ba-Zn type stabilizer.

The aforesaid mixture was kneaded on a roll and a sheet of thickness 1 mm was created. A light resistance test was performed on this sheet in a weatherometer. The result is shown in Table 2.

Table 2

Number	Material	Time exposed to radiation before deterioration, hours
Reference example 1-1	Tinuvin-P*	480
Example 1-1	No. 1 (Table 1)	680
Example 1-2	No. 2 (Table 1)	700
Example 1-3	No. 7 (Table 1)	640
Example 1-4	No. 8 (Table 1)	780
Example 1-5	No. 10 (Table 1)	810
Example 1-6	No. 11 (Table 1)	640
Example 1-7	No. 17 (Table 1)	640
Example 1-8	No. 20 (Table 1)	700
Example 1-9	No. 23 (Table 1)	610
Example 1-10	No. 24 (Table 1)	640
Example 1-11	No. 30 (Table 1)	660

* UV absorber made by Ciba-Geigy

Example 2

Polypropylene	100 parts
Dilauryl thiodipropionate	0.3 parts
Goodlite 3114*	0.1 parts
Test material (Table 3)	0.1 parts

*Phenolic antioxidant made by Goodrich Corp.

The aforesaid mixture was kneaded on a roll, then pressed to produce a sheet of thickness 0.5 mm. A light resistance test was performed on this sheet in a weatherometer. The result is shown in Table 3.

Table 3

Number	Material	Alteration time, hours
Reference Example 2-1	Tinuvin-P*	640
Reference Example 2-2	2-hydroxy-4-octoxybenzophenone	500
Example 2-1	No. 1 (Table 1)	810
Example 2-2	No. 2 (Table 1)	890
Example 2-3	No. 3 (Table 1)	840
Example 2-4	No. 9 (Table 1)	780
Example 2-5	No. 13 (Table 1)	840
Example 2-6	No. 16 (Table 1)	750
Example 2-7	No. 17 (Table 1)	810
Example 2-8	No. 18 (Table 1)	770
Example 2-9	No. 21 (Table 1)	840
Example 2-10	No. 31 (Table 1)	780
Example 2-11	No. 35 (Table 1)	770

Example 3

Ethylene - vinyl acetate copolymer* 100 parts

Test material (Table 4) 0.2 parts

*'Ultrathene UE 630' made by Nippon Polychemicals

The aforesaid mixture was kneaded on a roll at 120°C, then pressed at 120°C to produce a sheet (thickness 1 mm). A light resistance test was performed on this sheet in a weatherometer, and residual percentage strength was measured after 500 hours.. The results are shown in Table 4.

Table 4

Number	Material	Residual percentage strength
Reference Example 3-1	2-hydroxy-4-octoxybenzophenone	68%
Example 3-1	No. 1 (Table 1)	88%
Example 3-2	No. 4 (Table 1)	80%
Example 3-3	No. 8 (Table 1)	78
Example 3-4	No. 10 (Table 1)	78
Example 3-5	No. 14 (Table 1)	75
Example 3-6	No. 15 (Table 1)	80
Example 3-7	No. 17 (Table 1)	83
Example 3-8	No. 18 (Table 1)	81
Example 3-9	No. 24 (Table 1)	84
Example 3-10	No. 33 (Table 1)	82

Example 4

Liquid paraffin 100 parts

Test material (Table 5) 0.2 parts

UV transmittance of the liquid paraffin was measured using light of wavelength 330 nm
 (transmittance against air, using path length of 10 mm as standard cell).

The results are shown in Table 5.

Table 5

Number	Material	Transmittance
Reference example 4-1	None	96%
Example 4-1	No. 1 (Table 1)	7%
Example 4-2	No. 17 (Table 1)	6.8
Example 4-3	No. 23 (Table 1)	5.4

Number	Material	Transmittance
Example 4-4	No. 24 (Table 1)	5.7
Example 4-5	No. 29 (Table 1)	5.5
Example 4-6	No. 30 (Table 1)	5.6
Example 4-7	No. 32 (Table 1)	5.5

Example 5

In order to see inhibition effects with respect to deterioration of the organic material composition due to contact with heavy metal, a polypropylene film of thickness 0.5 mm containing copper fine powder was processed for 8 minutes at 180 °C with a mixing roll, then press-moulded for 5 minutes under conditions of 200 kg/cm² and 180 °C. Thermal deterioration of this sheet film was performed at 150.5 °C in a 'Hot Park Oven' (? characters difficult to read: no likely name found) in air, and the time when it became discolored or brittle was taken as the deterioration time. The results are shown in Table 6.

(Mixture)

Unstabilised polypropylene resin	100 parts
Topanol CA*	0.20 parts
Distearyl thiodipropionate	0.3 parts
Trinonylphenylphosphate	0.1 parts
Fine copper powder	1.0 parts
Test material (Table 6)	0.50 parts

*Phenolic antioxidant made by ICI Co. Ltd. UK

Table 6

No	Sample	Start of Deterioration, hours
Reference Example 5-1	None (no copper)	5
5-2	None	<1
5-3		5
5-4		5

No	Sample	Start of Deterioration, hours
Example 5-1	No 1 (table 1)	42
5-2	No 2 (table 1)	48
5-3	No 5 (table 1)	60
5-4	No 6 (table 1)	54
5-5	No 12 (table 1)	72
5-6	No 19 (table 1)	48
5-7	No 22 (table 1)	60
5-8	No 25 (table 1)	42
5-9	No 27 (table 1)	48
5-10	No 28 (table 1)	54
5-11	No 34 (table 1)	49

Example 6

A blend of the following was prepared in a mixer in this example under dry conditions for 10 minutes.

(Mixture)

Unstabilised polypropylene resin	100 parts
Irganox 1010	0.10 parts
(Phenolic antioxidant made by Swiss Chiba-Geigy)	
Dilauryl thiodipropionate	0.3 parts
Test material (Table 7)	0.4 parts

Here, a fine powder of the test material, average 5 microns, was used. This blend was compounded by extrusion at 245°C using a 30 micrometer extruder (rotation rate 301 rpm).

This compound was compression moulded at 180 °C, 200 kg/cm², for 5 minutes to create a sheet 0.5 mm thick. This sheet was cut to 40 x 50 mm, and made into a sandwich between an upper and lower foil of rolled copper 0.03 mm thick, and a 145g load was applied to the whole uniformly, to make it adhere, and a thermal deterioration test in contact with the

copper foil was performed at 150.5 °C in a 'Hot Park Oven' (? characters difficult to read: no likely name found) in air. Here, dispersibility was determined visually, and ones with excellent transparency are shown with double circle OO, good with single circle O, and ones dotted unsatisfactory parts are shown with x. The results are shown in Table 7.

Table 7

No	Sample	deterioration time, hours	dispersibility
Reference Example 6-1	None (no copper foil)	140	OO
6-2	None	96	OO
6-3		168	x
Example 6-1	No 1 (table 1)	1310	OO
6-2	No 4 (table 1)	1240	O
6-3	No 5 (table 1)	1200	OO
6-4	No 9 (table 1)	1240	O
6-6	No 10 (table 1)	1380	OO
6-6	No 15 (table 1)	1120	O
6-7	No 17 (table 1)	1270	OO
6-8	No 20 (table 1)	1310	OO
6-9	No 23 (table 1)	1180	OO
6-10	No 24 (table 1)	1310	OO
6-11	No 35 (table 1)	1280	OO

Example 7

For polyethylene which is often used to cover copper and the like, the results using the following compounded material were tested by forcing in copper powder.

That is to say, the following blend

Hizex 5100E*

100 parts

Fine copper powder 1.2
 Test material (Table 8) 0.3

(*stabilized medium low density polyethylene made by Mitsui Sekiyu Kagaku) was kneading processed using a mixing roll, then compression moulded at 150 °C, 200 kg/cm², for 5 minutes to create a sheet 0.5 mm thick. A thermal deterioration test was performed on this sheet film at 148°C in a 'Hot Park Oven' (? characters difficult to read: no likely name found) in an air environment. Deterioration start time was the time for it to become a discoloured grease.

The results are shown in Table 8

Table 8

Number	Material	Hours to start of deterioration
Reference Example 7-1	None	18
Example 7-1	No. 2 (Table 1)	284
Example 7-2	No. 6 (Table 1)	306
Example 7-3	No. 7 (Table 1)	256
Example 7-4	No. 8 (Table 1)	
Example 7-5	No. 10 (Table 1)	464
Example 7-6	No. 18 (Table 1)	330
Example 7-7	No. 19 (Table 1)	292
Example 7-8	No. 21 (Table 1)	480
Example 7-9	No. 23 (Table 1)	342
Example 7-10	No. 28 (Table 1)	268
Example 7-11	No. 32 (Table 1)	332

Example 8

Organic compound material is used again and again coloured. In particular, a large proportion of pigments are used.

Among the commonly used pigments, they may be present in the form of a coordination compound with a heavy metal, and this form can contribute to deterioration of organic materials. This example is one in which the degree of deterioration with respect to pigment is tested by the following method. That is to say, a film was created from the blend mentioned in Example 5 (Test table 9) by processing, adding 0.2 parts of copper phthalocyanine blue per 100 parts of the compound, mixing and kneading with a roll mill at 180 °C for 5 minutes, and compression moulding for 5 minutes at 180 °C and 200 kg/cm² to form a sheet 0.5 mm thick.

This sample piece (10 x 20mm), 10 sheets, was tested by heating in a Geer's oven in an air atmosphere at 160 °C, and the time for 5 or more of the sheets of the same sample to discolour was taken as the deterioration start time.

The results are shown in Table 9

Table 9

Number	Material	Hours to start of deterioration
Reference Example 8-1	None	72
Example 8-1	No. 1 (Table 1)	480
Example 8-2	No. 2 (Table 1)	420
Example 8-3	No. 3 (Table 1)	386
Example 8-4	No. 4 (Table 1)	340
Example 8-5	No. 5 (Table 1)	404
Example 8-6	No. 9 (Table 1)	392
Example 8-7	No. 12 (Table 1)	328
Example 8-8	No. 14 (Table 1)	374
Example 8-9	No. 25 (Table 1)	386
Example 8-10	No. 33 (Table 1)	368

Example 9

A sheet was prepared using the following mixture in accordance with the method of Example 5.

ABS resin (Blendex 111)	100 parts
Zinc stearate	0.5 parts
Titanium dioxide	5.0 parts
Test material (table 10)	0.5 parts

Then, copper foil was adhered in the same way, and the thermal test was performed in the oven in an air atmosphere for 1 hour at 180 °C.

The results are shown in the following Table 5 (sic). The following symbols are used for recording the colour.

- +++++ (very deep colour)
- ++ (some colour)
- + (pale yellow colour)

Table 10

Number	Material	Coloration
Reference Example 9-1	None	+++++
Example 9-1	No. 1 (Table 1)	++
Example 9-2	No. 5 (Table 1)	+
Example 9-3	No. 6 (Table 1)	+
Example 9-4	No. 19 (Table 1)	++
Example 9-5	No. 22 (Table 1)	+
Example 9-6	No. 25 (Table 1)	++
Example 9-7	No. 35 (Table 1)	++

Example 10

A test material, obtained by mixing zinc oxide 50 parts, stearic acid 1.0 part, fine copper powder 1.0 part, phenyl beta-naphthylamine 1.0 part and test material (Table 11) 5 parts into natural rubber 100 parts, was subjected to an ageing test under 760 mm oxygen pressure at

128 °C.

The time at which oxygen absorption occurred suddenly was determined as deterioration start time, and the time at which it reached 50ml/g is shown as the deterioration time.

The results are shown in the following Table 11.

Table 11

Number	Material	Deterioration start time
Reference Example 10-1	None	<25 minutes
Example 10-1	No. 6 (Table 1)	394
Example 10-2	No. 7 (Table 1)	346
Example 10-3	No. 8 (Table 1)	372
Example 10-4	No. 10 (Table 1)	372
Example 10-5	No. 10 (Table 1)	394
Example 10-6	No. 23 (Table 1)	322
Example 10-7	No. 32 (Table 1)	354

Example 11

A sheet of 1.0 mm thickness was prepared from the following blend, in order to see the results of a metal inactivator in accordance with this invention on polyvinyl chloride resin containing yellow copper powder. Test pieces of 10 x 20 mm were prepared from this, and an accelerated heat test was performed in air at 190 °C. The results are shown in Table 12.

Here, the deterioration start time is the time until blackening occurs.

Vinyl chloride resin	100 parts
DOP	48
Epoxidised soybean oil	2
Yellow copper powder	25
Zn stearate	0.3
Ca stearate	0.5

Mg stearate 0.5

Test material (Table 12)

Table 12

Number	Material	Deterioration start time
Reference Example 11-1	None (no yellow copper powder)	60 minutes
11-2	None	15 minutes
Example 11-1	No. 1 (Table 1)	60 minutes
Example 11-2	No. 2 (Table 1)	75 minutes
Example 11-3	No. 7 (Table 1)	60 minutes
Example 11-4	No. 11 (Table 1)	75 minutes
Example 11-5	No. 15 (Table 1)	60 minutes
Example 11-6	No. 20 (Table 1)	60 minutes
Example 11-7	No. 26 (Table 1)	75 minutes
Example 11-8	No. 29 (Table 1)	60 minutes

Example 12

Hydrocarbon oils are classified as "relatively low boiling point" hydrocarbon oil (for example, gasoline, kerosine and gas oil) and "relatively high boiling point oil" (for example, hydraulic oil and lubricating oil). Normally, metal inactivators are added to relatively low boiling point oil in a range of 1-10 ppm, and to relatively high boiling point oil in a range of 10-100 ppm. Here, kerosine oil was tested.

(Mixture)

Commercial kerosine	100 parts
Stabilizer	0.01
Ferric chloride	0.005

Finely powdered stabilizer of effectively 0.02 parts was dissolved in 100 volume parts of

kerosine, then the ferric chloride was added to create a mixture. This was transferred to a 500 volume parts cylinder, and was sealed with oxygen replacement. These vessels were left to stand for 40 days in a chamber at 40 °C, it was taken into an 0.1 mm salt cell and the infrared absorption spectrum was measured. When the compound of the aforesaid Synthesis Example 5 was added to this, there was almost no carbonyl absorption, but when the test compound was not added, it increased greatly.

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